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INTERURETHANE HYDROGEN BONDING IN THERMOPLASTIC
POLYURETHANE ELASTOMERS(U) MASSACHUSETTS UNIV AMHERST
DEPT OF POLYMER SCIENCE AND ENGINE. W J MACKNIGHT
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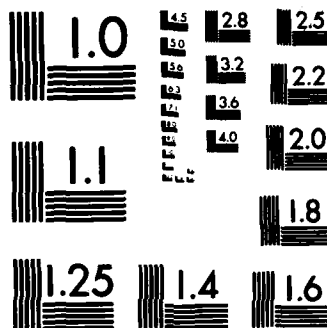
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FINAL REPORT
FOR
GRANT DAAG-29-80C-0054

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Statement of the Problem

→ The nature of hydrogen bonding, phase segregation, and hard segment organization was studied in a series of segmented polyurethanes based on hydroxy terminated polybutadiene (HTPBD) soft segments and hard segments consisting of either 2,4- or 2,6-toluene diisocyanate (TDI) and 1,4-butanediol (BDL). ←

Summary of Results

The existence of two phase morphology was deduced from dynamic mechanical relaxation and thermal analysis. All polymers exhibited a soft segment glass transition very close to T_g of free HTPBD homopolymer and independent of hard segment structure and concentration. The high temperature transitions, corresponding to the glass transition in 2,4-TDI polymers and melting in the 2,6-TDI polymers, were strongly dependent upon hard segment concentration and average hard segment length. An inversion of the continuous and dispersed phases was reflected in both stress-strain and dynamic mechanical properties above a 40 weight percent of hard segment. Thermal history was found to have a negligible effect on the position of the soft segment glass transition and, therefore, on the degree of phase segregation for all materials studied. The time dependence of dynamic mechanical and thermal properties was related to physical changes within the hard segment domains, independent of the soft segment matrix. An analysis of hydrogen bonding in a selection of HTPBD polyurethanes and model

compounds based on 2,4- and 2,6-TDI and p,p'-diphenyl-methane diisocyanate (MDI) and BDL hard segments was made using Fourier Transform Infrared Spectroscopy (FTIR). Changes in the frequency, halfwidth and intensity of the bonded N-H absorption band resulting from thermal treatment were correlated to structural changes as evidenced by differential scanning calorimetry (DSC); variations in behavior were related to differences in packing and the ability and ease of crystallization and reorganization of the hard segment repeat unit occurred. Resolution of the N-H band into its hydrogen bonded and non-bonded components indicated 80 to 90 percent of the N-H groups were hydrogen bonded at room temperature. Since hydrogen bonded interactions are limited to the hard segment components in PBD-containing polyurethanes, the results provide a quantitative measure of the extent of microphase separation. Temperature-dependent studies indicate that the onset temperature for hydrogen bond dissociation occurred at 25 to 75°C in the 2,4-TDI polymers and at about 130°C in the 2,6-TDI polymers, close to the transition temperatures for the amorphous and crystalline domain structure, respectively. Heat of dissociation was about 4 kcal/mole for the former series and 7-8 kcal/mole for the latter. Overall, the results indicated the thermal behavior of hydrogen bonding is sensitive to structure organization and correlate well with other properties studied via calorimetry and dynamic mechanical relaxation.

Publications

1. Polym. Eng. and Sci., 21(3), 163 (1981) (with C.M. Brunette, S.L. Hsu and N.S. Schneider)
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"Hydrogen-Bonding Properties of Hard-Segment Model Compounds in Polyurethane Block Copolymers."
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"Thermal Transition and Relaxation Behavior of Polybutadiene Polyurethanes Based on 2,6-Toluene Diisocyanate/"

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